▌ **Organometallic Chemistry**
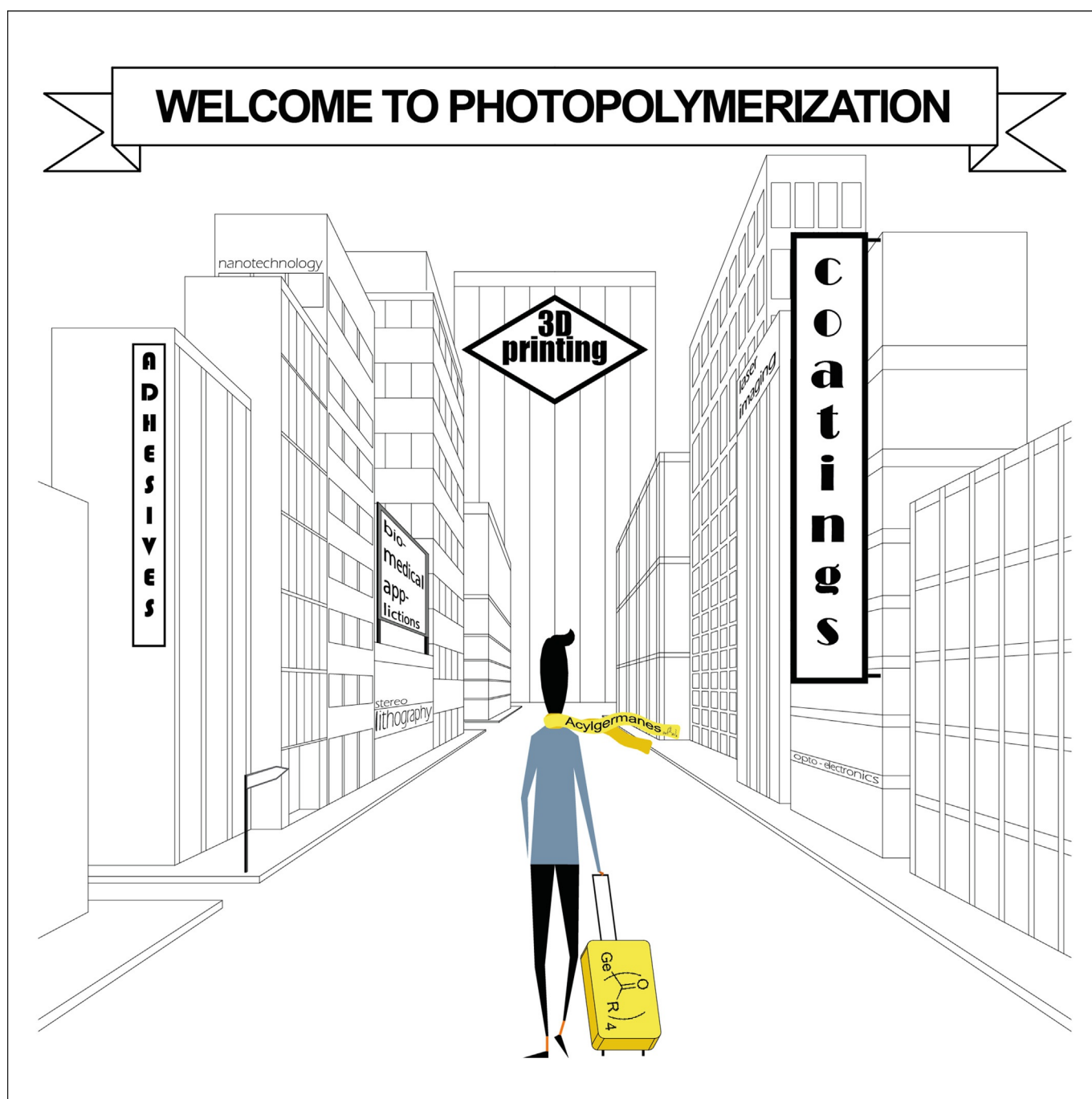
# Recent Advances in Germanium-Based Photoinitiator Chemistry

Michael Haas,[a] Judith Radebner,[a] Anna Eibel,[b] Georg Gescheidt,[b] and Harald Stueger*[a]

*Dedicated to Professor Norbert Moszner on the occasion of his 65th birthday*

**Abstract:** Acylgermanes provide an outstanding photoinduced reactivity at very useful absorption wavelengths. This encouraged multidisciplinary research groups to utilize them as highly effective and non-toxic photoinitiators particularly for medical applications. In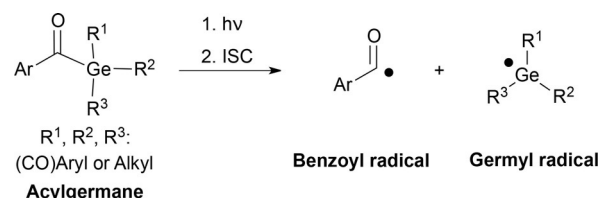 this Minireview, we present the most recent breakthroughs to synthesize acylgermanes. We also outline mechanistic aspects of photoinduced reactions of several acylgermane derivatives based on fundamental spectroscopic insights. These studies may aid future developments for tailor-made photoinitiators.

## Introduction

In the last decades the demand and application of high performance photochemically produced polymers has been immensely growing. Nowadays, their use is no longer restricted to the manufacture of micro-electronic devices, coatings, adhesives, inks, printing plates, optical waveguides but also enters fields of medicine (dental filling materials, artificial tissue, heart valves etc.) and fabrication of 3D objects.[1, 2] In the world of photopolymerization, high demands on the performance of the products exist. Moreover, they have to be produced by sustainable, economic and environmentally friendly procedures. To meet the strict qualifications, especially for medical applications, new types of non-toxic photoinitiating systems are necessary.

Upon absorption of light, the photoinitiating system (consisting of the photoinitiator and/or coinitiator and/or sensitizer) produces reactive species starting the polymerization process. These reactive species may be free radicals as well as ions (e.g. in cationic photopolymerization), generated from one-component (type I), two-component (type II) or multicomponent systems.[3] Type I photoinitiators (PIs) are molecules undergoing triplet-state homolytic bond cleavage, typically featuring a benzoyl moiety as the chromophore.[4] Examples include aryl ketones (e.g. benzoin ether or ester derivatives, α-hydroxy- and α-amino ketones), acylphosphane oxides as well as acylgermanes (Scheme 1).[5] The photochemistry and photophysics of aryl ketones and acylphosphane oxides have been investigated in detail by Turro and co-workers[6, 7] as well as by Wirtz, Dietliker, Gescheidt and co-workers (acylphosphane oxides).[8]

Type II PIs on the other hand, work in a bimolecular process together with a coinitiator. The initiating radicals are produced either by direct hydrogen abstraction between the excited PI and the coinitiator (a hydrogen donor) or by electron transfer

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Scheme 1. Photocleavage of type I PIs on the example of acylgermanes. A benzoyl-type radical and a germyl-type radical are formed via α-cleavage from the excited triplet state following photoexcitation and intersystem crossing (ISC).

followed by a proton transfer, which is more common. The light absorbing molecules in type II systems are usually based on benzophenone, thioxanthone, camphorquinone, anthraquinone, benzil or ketocumarin derivatives. Typical coinitators are amines, alcohols, or silanes serving as the electron donor and/or hydrogen source.[4] In addition, organogermanium hydrides have been described as efficient germanium-based coinitiators for type II PIs.[9] Scheme 2 shows the type II initiation process with the champhorquinone/amine system serving as a paradigm which has been widely applied in the field of dental fillings.[10]

An efficient photoinitiator features a good match between its absorption lines and the emission spectrum of the utilized light source. A high quantum efficiency for radical formation and a high reactivity of the resulting radicals towards the monomers are additional important requirements. In general, type I PIs are most widely applied, due to higher efficiency and decomposition rates when compared to type II initiators.[11] However, type II initiators often show more favorable visible-light absorption properties.[11] Nowadays, visible light initiation systems are highly desired, for reasons of high penetration depth of the incident light, biocompatibility and cost-effective irradiation sources. An overview of various types of visible light sensitive photoinitiating systems is given by Lalevée and co-workers.[12]
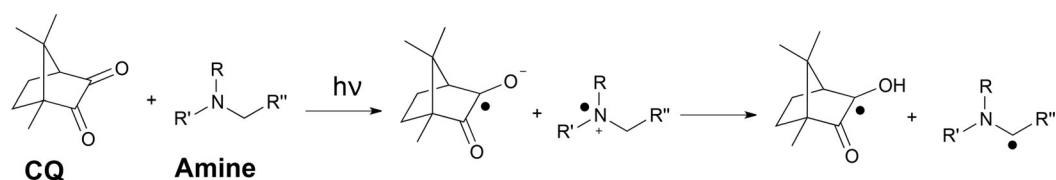
The development of type I visible light PIs is thus of paramount importance and has become a growing field of research. Apart from the above-mentioned factors, good solubility in aqueous media, biocompatibility and storage stability are crucial for modern (biomedical) applications such as tissue engineering or the preparation of hydrogel-type materials. Concerning water solubility, immense progress has been made with functionalized acylphosphane oxides by Grützmacher and co-workers.[13–15] Several acylphosphane oxides have been reported as being toxic and not suitable for applications such as dental fillings.[16] Compared to phosphorous-based PIs, currently known acylgermanes offer the advantage of reduced toxicity

**Scheme 2.** Initiation mechanism of a type II initiator on the example of a campherquinone/amine system. Electron transfer is followed by proton transfer, producing the CQ ketyl radical and an α-aminoalkyl radical.

as well as a significant red-shift of the longest-wavelength absorption bands.

Promoted by their outstanding absorption properties and their ability to efficiently produce reactive radicals (see Scheme 1), acylgermanes have become a promising class of photoinitiators.[17–19] Mono- and bisacylgermanes have first been reported as photoinitiators in 2008.[20, 21] Since then, substantial efforts have been made by several working groups to

elucidate the photoreactivity and preparation of acylgermanes.[18, 19, 22–26]

This Minireview focuses on the synthetic aspects and the photoreactivity of mono- to tetraacylgermanes as a promising class of visible-light type I PIs.

## The Beginning of Acylgermanium Chemistry

Acylgermanes were first synthesized by Brook and co-workers via hydrolysis of α,α-dibromoalkylgermanes [Eq. (1)].[27]
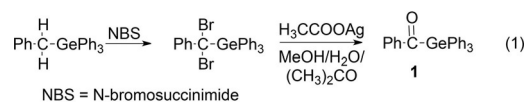


Concerning the synthetic methods towards mono-,[28–30] bis-, and trisacylgermanes,[31, 32] several methods have been reported throughout the last decades. However, the compounds ob-

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tained were not investigated with respect to their photoinitiating properties. The resurgence of interest in acylgermanium chemistry lately is mainly based on the advantageous photocleavage of the Ge−(CO) bond which has been overlooked for a long time. The development of novel and efficient synthetic strategies towards functionalized acylgermanes has evolved since then.

## Synthesis of Germanium-Based PIs

### Monoacylgermanes

The most common types of monoacylgermanes investigated as PIs are summarized in Scheme 3.
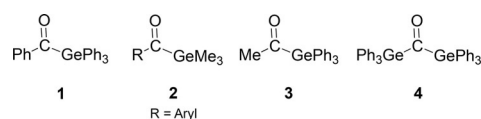


**Scheme 3.** Substitution patterns of acylgermanes investigated as PIs.

In 2008 and 2016 benzoyl germanium derivatives **2** were introduced as PIs for visible-light curing[2,19,21] with excellent efficiency in dental composites. These monoacylgermanes were synthesized from hexamethyldigermane and the respective acid chlorides in the presence of a Pd-catalyst and triethyl phosphite [Eq. (2)].[33]
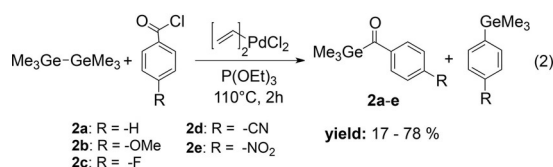


High photoinitiating ability was also reported for the acylgermanes **1** and **3**.[26] Compounds **1** and **3** are most conveniently prepared from the reaction of Ph$_3$GeLi with the appropriate ester [Eq. (3)][29] or from the corresponding germyl-1,3-dithiane [Eq. (4)].[30]
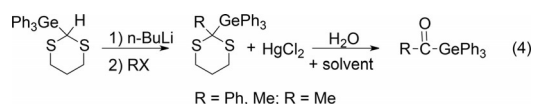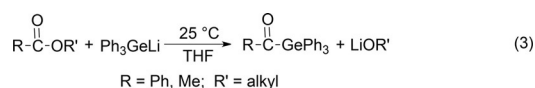




For the bisgermyl derivative **4** a substantial red-shifted absorption and a high polymerization ability under visible light irradiation was observed.[34] The synthesis of **4** was accomplished by the oxidation of bis(triphenylgermyl)methanol with dicyclohexylcarbodiimide/pyridinium trifluoroacetate in DMSO [Eq. (5)].[35]
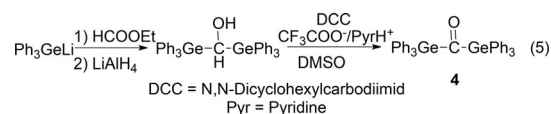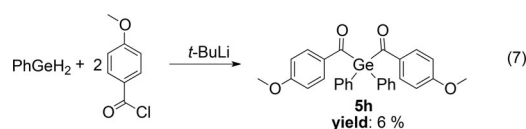


### Bisacylgermanes

Almost concurrently with the introduction of monoacylgermanes as promising PIs, bisacylgermanes were studied. In this context, the bisacylgermanium derivatives **5 a**–**g** were synthesized by a Corey–Seebach type reaction, which was adapted for higher homologues of carbon by A. Brook [Eq. (6)].[20,21,30,36]
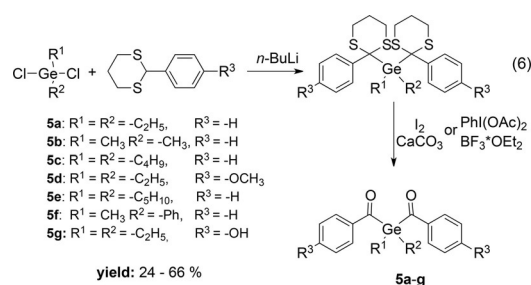


In the case of the sterically encumbered bisacylgermane **5 h** the dithiane route failed. Thus, compound **5 h** was alternatively prepared by the acylation of diphenylgermane though the low yield prevented complete characterization [Eq. (7)].[36]



Based on the synthetic approach presented in Equation 6 the first bisacylgermane was implemented as a commercially available photoinitiator [bis(4-methoxybenzoyl)diethylgermane, Ivocerin®]. Ivocerin® and related bisacylgermanes show significantly enhanced extinction coefficients compared to monoacylgermanes resulting in reduced curing times and increased curing depth of the final composite material.[22,36,37] Beside of these benefits, Ivocerin® still suffers from inefficient curing depths at wavelengths >450 nm.[20] Additionally, the multistep synthesis and the tedious purification cause high production costs and prevent, so far, the application as a PI apart from dental composites.
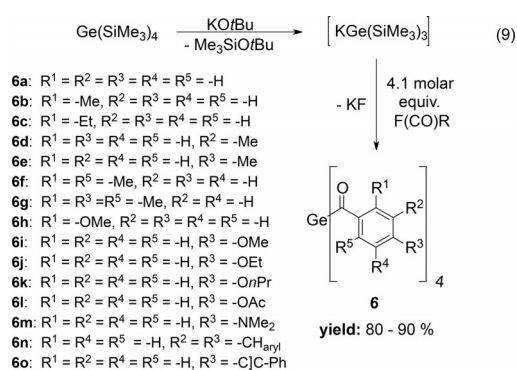
### Tris- and tetraacylgermanes

One trisacylgermane derivative was prepared from PhH$_2$GeLi and Cl-(CO)Mes and reported in 1992 [Eq. (8)],[31] however, without discussing its photoinduced reactions.

$$3\ PhH_2GeLi + 3\ Mes\!-\!\overset{O}{\underset{Cl}{\big\langle}} \xrightarrow{-\ 3\ LiCl} PhGe\!\left[\overset{O}{\underset{Mes}{\big\rangle}}\right]_3 + 2\ PhGeH_3 \quad (8)$$
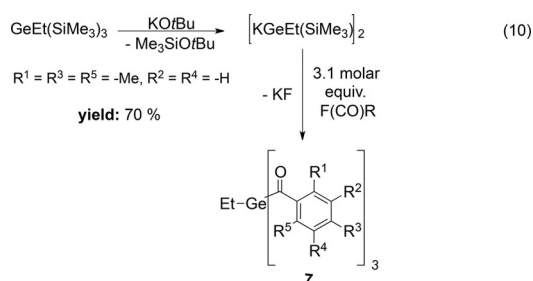
Mes = 2,4,6-trimethylphenyl

Recently, the chemistry of tris- and tetraacyl substituted germanes and their ability to serve as long-wavelength PIs was investigated.[16,23,24] In the course of these studies a synthetic protocol allowing a straightforward access to these highly desirable compounds was developed [Eq. (9)].

$$Ge(SiMe_3)_4 \xrightarrow[-\ Me_3SiOtBu]{KOtBu} \big[KGe(SiMe_3)_3\big] \quad (9)$$

**6a**: R$^1$ = R$^2$ = R$^3$ = R$^4$ = R$^5$ = -H
**6b**: R$^1$ = -Me, R$^2$ = R$^3$ = R$^4$ = R$^5$ = -H
**6c**: R$^1$ = -Et, R$^2$ = R$^3$ = R$^4$ = R$^5$ = -H
**6d**: R$^1$ = R$^3$ = R$^4$ = R$^5$ = -H, R$^2$ = -Me
**6e**: R$^1$ = R$^2$ = R$^4$ = R$^5$ = -H, R$^3$ = -Me
**6f**: R$^1$ = R$^5$ = -Me, R$^2$ = R$^3$ = R$^4$ = -H
**6g**: R$^1$ = R$^3$ = R$^5$ = -Me, R$^2$ = R$^4$ = -H
**6h**: R$^1$ = -OMe, R$^2$ = R$^3$ = R$^4$ = R$^5$ = -H
**6i**: R$^1$ = R$^2$ = R$^4$ = R$^5$ = -H, R$^3$ = -OMe
**6j**: R$^1$ = R$^2$ = R$^4$ = R$^5$ = -H, R$^3$ = -OEt
**6k**: R$^1$ = R$^2$ = R$^4$ = R$^5$ = -H, R$^3$ = -OnPr
**6l**: R$^1$ = R$^2$ = R$^4$ = R$^5$ = -H, R$^3$ = -OAc
**6m**: R$^1$ = R$^2$ = R$^4$ = R$^5$ = -H, R$^3$ = -NMe$_2$
**6n**: R$^1$ = R$^4$ = R$^5$ = -H, R$^2$ = R$^3$ = -CH$_{aryl}$
**6o**: R$^1$ = R$^2$ = R$^4$ = R$^5$ = -H, R$^3$ = -C]C-Ph

4.1 molar equiv. F(CO)R, - KF

**6**
**yield:** 80 - 90 %

Based on the well-established multiple silyl group abstraction from (Me$_3$Si)$_3$SiK by fluorinated reagents,[38] the reaction of (Me$_3$Si)$_3$GeK[39,40] with 4.1 molar equivalents of acid fluorides F-(CO)R (R = aryl) leads to the formation of tetraacylgermanes **6** in >85 % yields (Equation 9). Trisacylgermanes are formed via the same mechanism upon treatment of (Me$_3$Si)$_2$EtGeK with the respective acid fluorides [Eq. (10)].

$$GeEt(SiMe_3)_3 \xrightarrow[-\ Me_3SiOtBu]{KOtBu} \big[KGeEt(SiMe_3)\big]_2 \quad (10)$$

R$^1$ = R$^3$ = R$^5$ = -Me, R$^2$ = R$^4$ = -H

**yield:** 70 %

3.1 molar equiv. F(CO)R, - KF

**7**

Contrary to the previously mentioned synthetic strategies towards acylgermanes, this protocol represents an easy-to-perform one-pot synthesis and the products can be isolated by simple recrystallization in excellent yields. Up to now, a variety of differently EDG-substituted tetraacylgermanes have been prepared.[18,24]

## Spectroscopic Properties of Germanium-Based PIs

### Absorption behavior

A good match between the emission spectra of the lamp and the absorption bands of a photoinitiator is essential to achieve

its preferential functionality. In this respect, aryl acylgermanes exhibit properties particularly suitable for long-wavelength visible-light curing processes. All aryl substituted acylgermanes show longest wavelength absorption bands with $\lambda_{max}$ values between 363 and 419 nm, tailing well into the visible region. These bands are significantly red-shifted and intensified as compared to other common PI systems such as aryl ketones or the well-established acylphosphane oxides.[13,27,41]

The longest wavelength absorption bands of acylgermanes were computationally assigned to the HOMO–LUMO transition and show considerable charge transfer character (compare Figure 1).[18] Upon excitation, electron density is displaced from
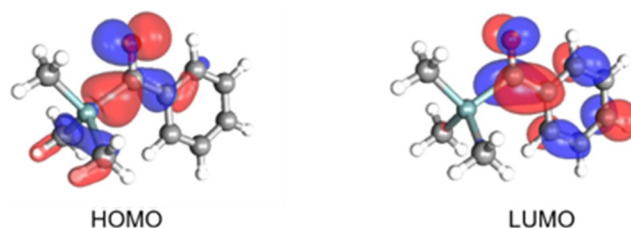


**Figure 1.** Frontier-orbitals of Me$_3$GeBz **2a**. Singlett excitations calculated at the PCM(MeCN) TD-DFT CAM-B3LYP/def2-TZVP//B3LYP/6-31+G(d,p) level of theory.

the n(C=O)/σ(Ge–C) bonding HOMO to the π*(C=O/Aryl) antibonding LUMO which results in the population of an orbital with antibonding character between the Ge–C bond. In analogy to related ketones, homolytic bond cleavage occurs upon intersystem crossing (ISC) via the excited triplet state.[7]

In line with literature data of simple aryl ketones, pronounced substituent effects on the absorption properties of aryl acylgermanes are observed. The introduction of electron withdrawing groups in *ortho*- or *para* positions at the aromatic ring induces a bathochromic shift of $\lambda_{max}$ and decreases the extinction coefficients. The opposite behavior is observed when electron donating groups are attached.[18,19,25,36] Figure 2 shows the effect of Me and OMe substitution on the absorption behavior of selected tetraacylgermanes. Additionally, the extinction coefficients increase almost linearly according to the number of chromophores attached to the germanium center (Figure 3).
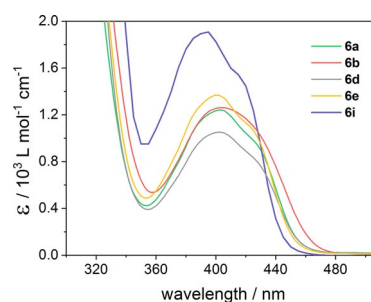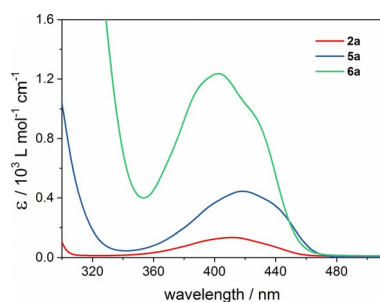


**Figure 2.** Absorption spectra of selected tetraacylgermanes (substituents at aromatic ring are stated in parentheses): **6a** (phenyl), **6b** (*o*-Me) **6d** (*m*-Me), **6e** (*p*-Me) and **6i** (*p*-OMe), (CH$_3$CN solution; $c = 10^{-3}$ mol L$^{-1}$).

**Figure 3.** UV/Vis spectra of a monoacylgermane **2a**, bisacylgermane **5a**, and tetraacylgermane **6a** ($CH_3CN$ solution; $c = 10^{-3}$ mol L$^{-1}$).

Di-*ortho*-substitution at the aromatic ring in aryl acylgermanes induces a significant hypsochromic shift of the longest wavelength absorption band. This hypsochromic shift roughly correlates with the twist (or dihedral) angle between the plane of the phenyl ring and the C=O moiety, which significantly deviates from a coplanar arrangement in the di-*ortho*-substituted derivatives caused by the steric repulsion between the *ortho*-substituents and the C=O group (compare Figure 4). This correlation is conclusive because larger values of the dihedral
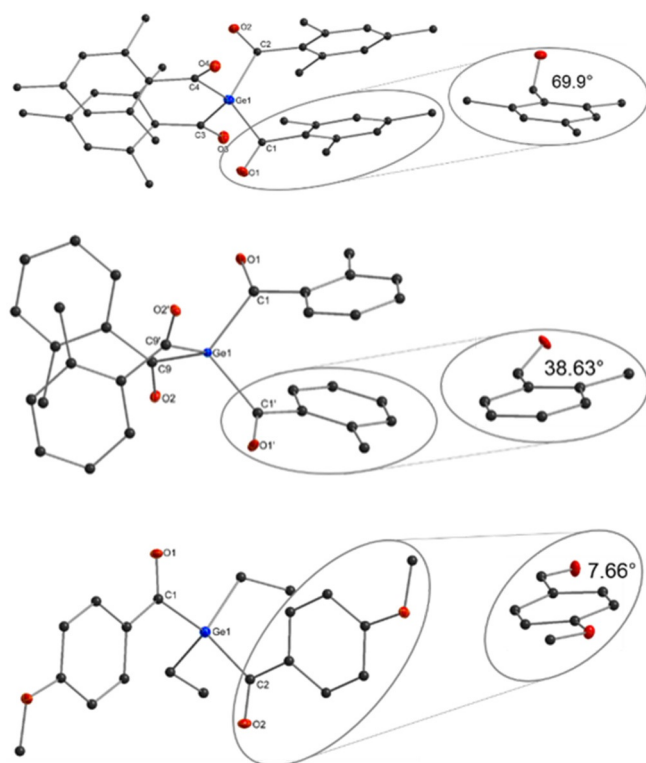


**Figure 4.** ORTEP representation of **6b,g** and **5d**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Mean torsion angles [°] are shown in the magnified part.

angle reduce phenyl/C=O $\pi$–$\pi$ conjugation thus increasing the HOMO–LUMO gap and shifting the corresponding UV maximum to the blue.

Table 1 shows $\lambda_{max}$ values and extinction coefficients for the longest wavelength absorption bands of all reported acylgermanes.

**Table 1.** $\lambda_{max}$ values and extinction coefficients for the longest wavelength absorption bands of monoacylgermanes **2a–d**,[19,21] bisacylgermanes **5a–5f**,[36] trisacylgermane **7**,[25] and tetraacylgermanes **6a–k**.[18,24]

| $\lambda_{max}/$ $\varepsilon$[L mol$^{-1}$ cm$^{-1}$] | | $\lambda_{max}/$ $\varepsilon$[L mol$^{-1}$ cm$^{-1}$] | | $\lambda_{max}/$ $\varepsilon$[L mol$^{-1}$ cm$^{-1}$] | |
|---|---|---|---|---|---|
| monoacylgermanes | | | | | |
| **2a** | 411.5/137 | **2c** | 405/[a] | **2e** | 429/[a] |
| **2b** | 397/[a] | **2d** | 425/[a] | | |
| bisacylgermanes | | | | | |
| **5a** | 418.5/ 490 | **5d** | 408.2/ 724 | **5g** | 406.2/ 686 |
| **5b** | 417.6/ 511 | **5e** | 418.1/ 568 | **5h** | 402.5/ 570 |
| **5c** | 418.5/ 529 | **5f** | 418.8/ 549 | | |
| tris- and tetraacylgermanes | | | | | |
| **7** | 383/1226 402sh/903 | **6f** | 374/ 1477 403sh/954 | **6l** | 400/1262 422sh/992 |
| **6a** | 403/1240 419sh/1050 | **6g** | 376/1475 | **6m** | [b] |
| **6b** | 407/1266 | **6h** | 400/1160 | **6n** | [b] |
| **6c** | 407/1258 | **6i** | 395/1897 413sh/1556 | **6o** | [b] |
| **6d** | 402/1058 | **6j** | 392/1708 415sh/1362 | | |
| **6e** | 400/1377 422sh/1113 | **6k** | 393/1765 414sh/1396 | | |

[a] not published; sh=shoulder. [b] Could not be detected due to overlapping of n–$\pi$* with $\pi$–$\pi$* bands.

In summary, the substituent effects described above allow tuning of the absorption properties of aryl acylgermanes. The most intense absorption at wavelengths $\geq 450$ nm is observed for the *ortho*-Me substituted tetraacylgermane **6b**. Hence, **6b** is of particular interest for applications with long-wavelength visible-light emitting sources.

## PI Performance

### Photochemistry of acylgermanes

Whereas, the photochemistry of acylsilanes has been investigated in great detail by Brook and co-workers and Porter and co-workers in the 1970s and 1980s,[39,42,43] only a few studies have been conducted concerning the photochemistry of acylgermanes. Their discovery serving as advantageous PIs has triggered extended mechanistic investigations.

Germyl radicals formed via photolysis of monoacylgermanes Ph$_3$Ge(CO)Ph and PhMe$_2$Ge(CO)Ph have been observed by Mochida and Hayashi in 1985 using laser-flash photolysis (LFP).[44] The assignment of the transient absorption bands to the Ge-centered radicals Ph$_3$Ge$^\bullet$ and PhMe$_2$Ge$^\bullet$ has been possible via comparison with the LFP spectra reported previously for Ge-centered radicals derived from germanium hydrides (1983 by Scaiano and Ingold as well as by Hayashi and Mochida).[45] Taraban and co-workers investigated the photocleavage of monoacylgermane Et$_3$Ge(CO)Ph (benzoyltriethylgermane) via chemically-induced dynamic nuclear polarization (CIDNP) NMR spectroscopy in 1987, confirming the formation of Et$_3$Ge$^\bullet$ and $^\bullet$(CO)Ph as the primary triplet radical pair.[46] The photochemical

reaction pathways of acylgermanes in polar and non-polar media have been found to be analogous to those reported for acylsilanes.[43,46,47]

Triplet-state α-cleavage of a Ge—(CO) bond has been confirmed as the major photochemical reaction pathway of bis-acylgermane **5 a** by Gescheidt and co-workers in 2013, as evident from time-resolved EPR (TR-EPR, CIDEP) spectroscopy as well as femto- and nanosecond transient absorption spectroscopy (see Scheme 1).[23] TR-EPR spectra of a bis- and a tetra-acylgermane are depicted in Figure 5.
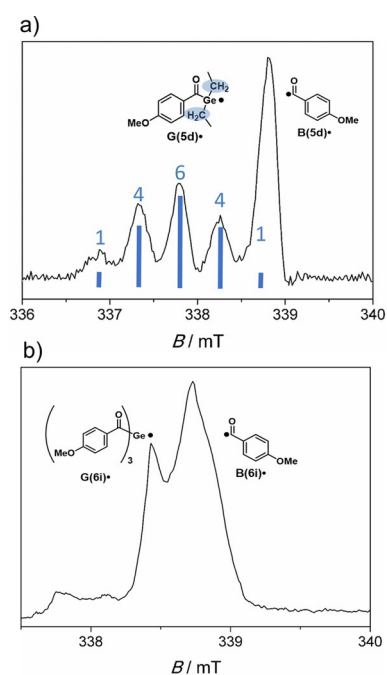


**Figure 5.** TR-EPR spectra recorded 300–400 ns after laser-flash photolysis (355 nm) of argon-saturated toluene solutions (10 mM) of a) **5 d** and b) **6 i**. Blue bars indicate the splitting of the germyl radical signal due to the four β-hydrogen atoms in radical **G(5 d)**.

The follow-up reactions of the primary radicals have been elucidated by ¹H CIDNP spectroscopy.[48] Scheme 4 shows a summary of the radical reaction pathways proposed on the basis of CIDNP experiments of acylgermanes in absence and presence of monomers.[18,23,25]

### Initiation efficiency

High quantum yields of decomposition are an important requirement for efficient photoinitiators. Quantum yields of mono- to tetraacylgermanes have been reported by our group recently, with values ranging from ≈0.4 (tetraacylgermanes) to ≈0.8–0.9 (bisacylgermanes).[25]

To achieve high curing depth and to avoid colored polymers, fast photobleaching of the PI at the irradiation wavelength is equally crucial, especially upon irradiation with visible light. This is particularly relevant for (bio)medical applications such as dental composites. Various photobleaching studies of acyl-germanes have been performed.[20,25,49]

Wavelength-dependent photobleaching curves are presented in Figure 6 for irradiation of mono- to tetraacylgermanes
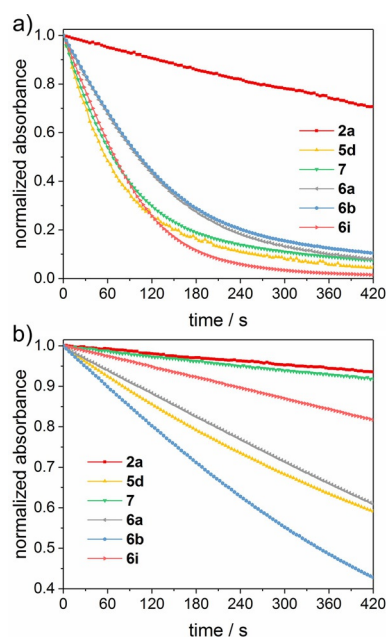


**Figure 6.** Steady-state photolysis of mono-, bis-, tris- and tetraacylgermanes in acetonitrile/MMA solutions. Plots of normalized absorbance versus time for irradiation at a) 385 nm and b) 470 nm, monitored at the n–π* absorption maxima (**2 a**: 412.5 nm, **5 d**: 409 nm, **7**: 383 nm, **6 a**: 404 nm, **6 b**: 405.5 nm, **6 i**: 393 nm).

with LEDs at 385 nm and 470 nm in acetonitrile/monomer solutions. The monomer (methyl methacrylate, MMA) acts as a radical trap, leading to the formation of photoproducts, which do not absorb in the visible wavelength range. Generally, photobleaching is more efficient upon irradiation with LED light at 385 nm than at 470 nm for all investigated compounds. Tetra-acylgermane **6 b** exhibits remarkably fast photobleaching upon irradiation at 470 nm, indicating efficient initiation under high-wavelength visible light.[25]

Apart from high decomposition quantum yields and efficient photobleaching, fast addition of the primary radicals to monomers is essential for an efficient photoinitiator. Laser-flash photolysis (LFP) is a powerful method for the analysis of radical-to-monomer addition kinetics. Lalevée and co-workers reinvestigated the transient absorption properties of the Ph₃Ge· radical in 2009, showing remarkably fast reactivity of this radical toward monomer double bonds (rate constants in the order of $10^8$ M⁻¹ s⁻¹).[26]

We studied the kinetics of various Ge-centered radicals derived from mono- to tetraacylgermanes toward a series of monomers.[23,25] A summary of the addition rate constants is given in Figure 7. Notably, Ge-centered radicals show significantly higher reactivity toward monomers than related phosphorus-based radicals derived from acylphosphane oxides.[15] Further efficiency studies of acylgermanes have been performed using photo-DSC, showing particularly high reactivity for bisacylgermane **5 d** and tetraacylgermane **6 b**.[18,49]
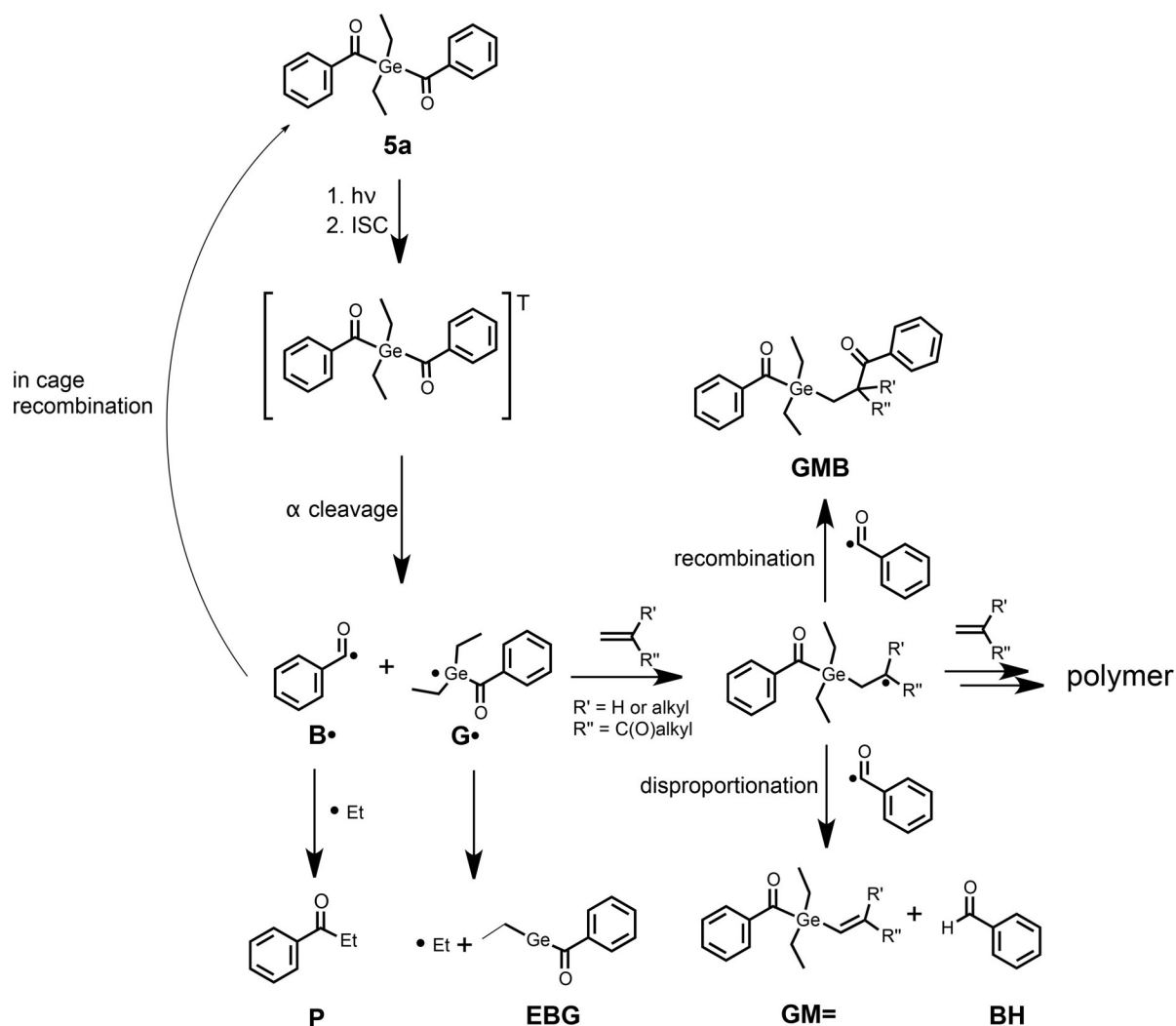
**Scheme 4.** Proposed reaction Scheme of initiator **5 a** in the presence of monomers, as established via CIDNP experiments.
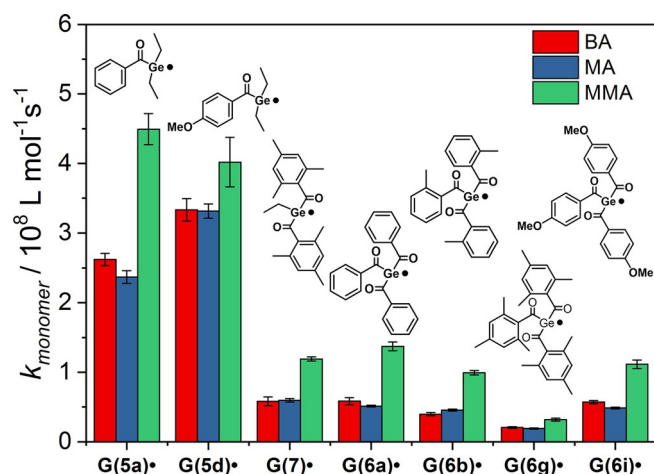


**Figure 7.** Second-order rate constants $k_{monomer}$ for the addition of **G·** to butyl acrylate (BA), methyl acrylate (MA) and methyl methacrylate (MMA).

## Conclusions

Acylgermanes have been shown to be highly efficient, non-toxic visible-light photoinitiators for radical polymerization. Recently, novel straightforward synthetic protocols have led to the preparation of tris- and tetraacylgermanes, completing the spectrum from mono- to tetrasubstituted derivatives. Functionalization on the aromatic rings allows fine-tuning the absorption properties and shifting the absorption bands towards the long-wavelength region. Fast photobleaching and high reactivity of the germanium-centered radicals towards monomer double bonds substantiate their high potential for various applications including photopolymerizable adhesives, coatings, or 3D-lithography techniques.

## Outlook

In the future, the development of acylgermanium derivatives with improved solubility in aqueous media will become a major challenge, broadening the range of potential applica-

tions. Further insights into the photoreactivity of acylgermanes will remain of great interest, in order to fully elucidate structure–reactivity relationships and to enable the design of derivatives with tailor-made absorption bands and initiation efficiency.

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## Conflict of interest

The authors declare no conflict of interest.

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